

Nitrogen Removal

Question

We have a station in the melt shop for stirring silicon killed steel in ladles with argon gas through porous plugs. Both argon and nitrogen are available for stirring. When the combined partial pressure of gasses exceeds 1.05 atm, the gas comes out of the liquid steel and pinholes or blowholes result. One would suppose that vigorous stirring with argon gas would help to remove nitrogen but normally we only remove a small amount of nitrogen, if any. Sometimes we actually see an increase in nitrogen. What is the phenomenon that is causing us to retain nitrogen? What steps we may take to lower nitrogen in liquid steel?

P.S. USA

Answer

You have touched on a sore subject for most steelmakers: nitrogen removal. Rather than removing the nitrogen, the preferred approach is to prevent nitrogen from entering the molten steel in the first place. This is done through proper furnace and tapping practices (and is the subject of many books and articles).

Given the presence of nitrogen, there are two processes which control the rate for nitrogen removal: chemical kinetics and mass transfer. Typically, chemical kinetics would prevail at lower temperatures and mass transfer would be the rate-controlling step at higher temperatures. For ladle denitrogenization in a silicon-killed steel, we need to examine both of these mechanisms. The chemical kinetics are most important when the oxygen and sulfur concentrations are high because they are both surface-active elements. In your case we will consider only sulfur (since the steel is killed oxygen is low). At sulfur levels above 0.006%, sulfur will impede nitrogen removal due to activity at the gas metal interface. In other words, even if the nitrogen can find its way to the top of the ladle, the gas-metal boundary is crowded with sulfur, thus inhibiting the reaction $2N \rightarrow N_{2(g)}$. At lower sulfur levels, mass transfer dictates the overall rate and mass transfer via the small amount of argon bubbled in the bottom of the ladle is limited.

Let's consider the difference between gas injection into the EAF and a ladle. When nitrogen is removed in the EAF via a

CO boil, it is done at higher temperatures and the boil is taking place with a gas purge that is 3 to 4 orders of magnitude greater than that in the ladle. This means that stirring activity (mass transfer coefficient) is correspondingly that much higher. There is simply not enough purge gas available in the ladle to remove significant amounts of nitrogen.

We should also consider equilibrium. In order to degas a melt, there must be a driving force pushing the desorption of the nitrogen. The greater the driving force, the more gas can be removed. This is why the most effective degassing is done under vacuum. However, even in the case of vacuum degassing under ideal conditions, there is a limit to nitrogen removal. The rate is dictated by the equilibrium relationship of the liquid and lower pressure atmosphere.

You also mentioned that an increase in nitrogen is sometimes observed. This may be caused by too vigorous a stir such that fresh metal is exposed to the atmosphere (sometimes called opening up an eye in the slag). This will allow air to become entrapped within the melt and absorb nitrogen. (Answer provided courtesy of Ken Grieshaber, Director, Metals Market Sector, Gases Americas, BOC Group, Murray Hill, NJ)